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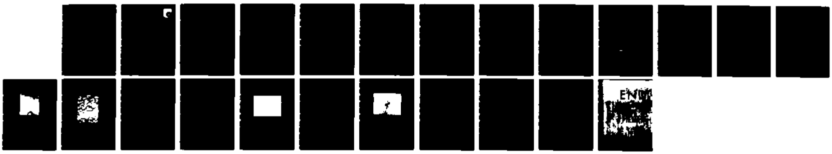

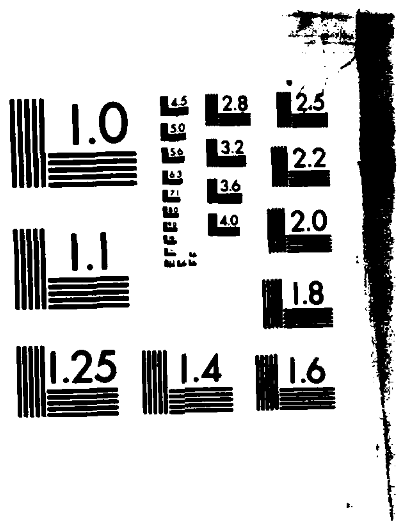

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REPLICATED CDTE SUBSTRATES

Radiation Monitoring Devices, Inc.
44 Hunt Street
Watertown, MA 02172

September 1983

Final Report for May 1982 - May 1983

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There is now a critical need for large numbers of high quality single crystal CdTe substrates for LPE growth of HgCdTe to use in infrared focal plane array sensors. The CLEFT crystal growth process, originally used to grow thin GaAs single crystals of solar cell applications, potentially offers a practical solution to this problem. Therefore, to investigate this unique crystal growth process further, a proof of concept research program was carried out to determine if this attractive technique could be applied to CdTe.

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The result of this research has been the growth of 1 cm^2 continuous CLEFT layer of CdTe over an appropriate CLEFT growth mask. This is proof that the needed lateral growth does occur for CdTe oriented in the (111) direction. The procedures used to achieve this are discussed in detail in this report.

SUMMARY

A research program has been carried out to investigate the unique CLEFT crystal growth technique for the preparation of CdTe LPE substrates. This technique should ultimately be able to reproducibly provide many excellent substrates from a single high quality seed crystal. The benefit would be reduced cost and increased availability of LPE substrates.

The results of this research on CLEFT growth of CdTe substrates clearly show that the CLEFT process does work for CdTe. We have demonstrated that CdTe will grow epitaxially from the vapor phase onto (111) oriented CdTe seed substrates and that the epilayer does grow laterally over a suitable growth mask. Further improvement in the mask deposition technique and optimization of the growth conditions should result in a technique for rapid and economical fabrication of high quality single crystal substrates suitable for LPE of HgCdTe infrared detectors.

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I. INTRODUCTION

It is now widely recognized that the next generation of HgCdTe infrared detector systems will be based on thin film, photovoltaic device arrays which are produced by epitaxial growth on suitable substrates. These arrays will have the advantages of rapid production, reliable output, integrated circuit technology and commensurately low cost. Of critical importance in any epitaxial growth technology is the quality (and availability) of the substrate material.

Because of its close lattice match and chemical similarity, CdTe has been the substrate material of choice for many researchers. HgCdTe films and devices prepared on CdTe substrates have demonstrated very high quality using several growth techniques. Liquid phase epitaxy (LPE), in particular, has been a growth method widely used with significant success. However, the primary limitation to LPE growth at the present time is the inability to obtain sufficient quantities of high quality substrates.

To address this problem a proof-of-concept research program was carried out to investigate the preparation of CdTe substrates using the CLEFT process (Cleavage of Lateral Epitaxial Films for Transfer). Under this program we have been able to demonstrate that the lateral epitaxial overgrowth of CdTe needed for producing CLEFT films does occur on (111) oriented substrates. Total lateral overgrowth has been achieved over an area larger than 1 cm2. Further development should result in a practical and reliable method to prepare suitable substrates for LPE growth of HgCdTe.

II. BACKGROUND

A. The Cleft Process - The CLEFT process was recently invented and developed at Lincoln Laboratories for the preparation of thin films of GaAs. It is basically a simple multi-step process which is outlined in Figure 1(1). A master substrate is prepared by applying a photoresist stripe pattern to the surface so as to leave exposed only small parallel regions of material. The remaining photoresist is converted to graphite in an oven at modest temperatures so as to reduce its adhesion to the newly grown layer yet retain the carefully formed pattern. Using a vapor phase epitaxial (VPE) growth system, the new layer nucleates and forms, starting at the exposed stripe areas. The crystal orientation and growth conditions are selected so that the lateral growth is enhanced relative to the vertical growth. This is a critical factor, since the lateral growth must be enhanced to permit continuous film formation.

Once the new layer is fully developed and is of the proper thickness, growth is halted and the film prepared for removal. Shown in Figure 2 is a schematic of the mechanism of removal(1). It simply involves bonding the film to a suitable substrate and mechanically removing the grown layer.

This remarkably simple process yields films of very high quality with little or no degradation due to cleavage. GaAs substrates have been reused as many as four times with no apparent reason why they cannot be reused even more. This same approach has also been used for InP(2) and clearly points to the generalization that many materials may be prepared this way, if the proper vapor phase growth conditions can be met.

B. Vapor Growth of CdTe - The attractiveness of the CLEFT process is that it places only one major requirement on the material to be grown. This requirement is that there exists a vapor phase growth system which enhances the lateral growth of the material in the desired crystalline orientation. In order to demonstrate that this is the case for CdTe, this program investigatd the closed tube halide transport system described by Paorici, et. al.(3).

Paorici's method uses a sealed ampoule and makes use of the transport mechanism shown in equation 1.

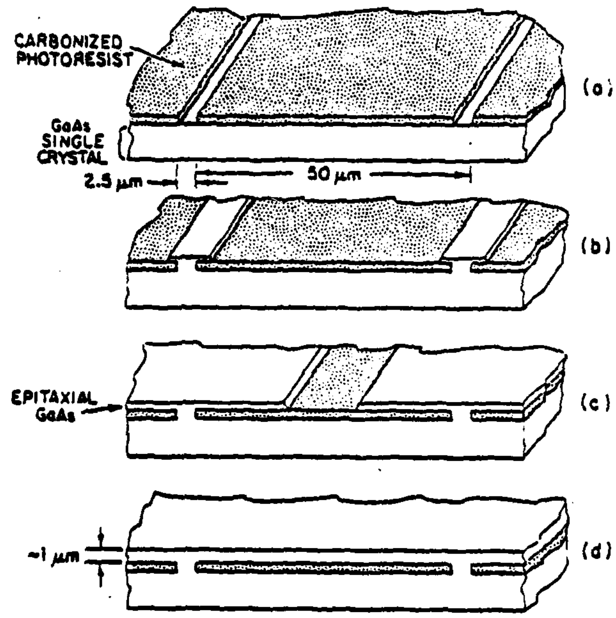


Figure 1. Lateral overgrowth from parallel slit openings in a carbonized photoresist growth mask. (a) the surface before growth begins, (b) and (c) intermediate stages of lateral growth, (d) continuous film. **(from Ref. 1)**

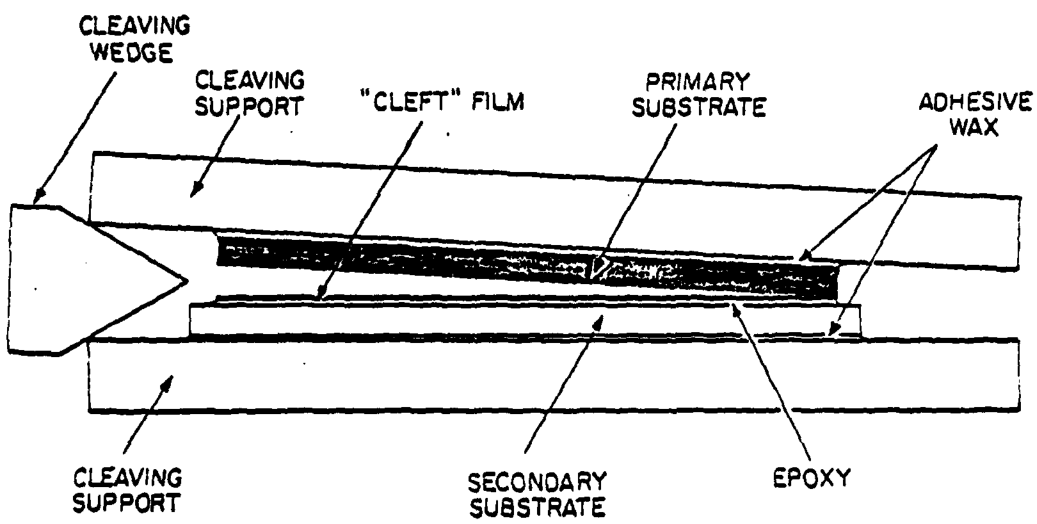


Figure 2. Procedures for cleaving the overgrowth film from the primary substrate and transferring it to a secondary substrate. **(from Ref. 1)**

(1) $CdTe(s) + 2HCl(g) \rightarrow CdCl_2(g) + H_2(g) + 1/2Te_2(g)$

In this process the halide transport agent (NH_4Cl) and the CdTe source material are positioned in hot zone of a 2 zone furnace. The source region at the ampoule is held at about 800oC and the growth region at about 650oC. Paorici was able to grow millimeter sized CdTe platelets with the flat surface parallel to the (111) plane. These platelets nucleated on the walls of the quartz ampoule. It was assumed that the same mechanism responsible for the growth of platelets would cause epitaxial growth to take place on a suitably prepared (III) oriented CdTe substrate. For these reasons methods very similar to the ones used by Paorici were considered appropriate for CLEFT studies.

To demonstrate CLEFT growth of CdTe, an appropriately masked CdTe substrate was positioned in the 650oC growth region.

III. CdTe GROWN BY CLEFT

A. Vapor Phase Transport Studies - The technique used for vapor phase growth at RMD is a modification of the one used by Paorici et.al.. Initial work on the program involved reproducing the results of these workers to determine if their method would be applicable to study CLEFT. A resistance heated tube furnace was constructed with the desired temperature gradient (source temp. = 800oC, substrate temp. = 650oC) and loaded with an ampoule containing high purity CdTe and NH_4Cl as the vapor source and a piece of polycrystalline CdTe as a substrate. The results of these experiments showed that while a substantial portion of the CdTe was transported to the region of the substrate, a large number of CdTe platelets also grew in the region of the substrate. A net increase in substrate mass occurred indicating that epitaxial growth had taken place. In short, the experiments verified that the methods used by Paorici as adopted by RMD seemed an appropriate vapor phase growth technique by which to study the CLEFT process with CdTe.

One factor that became evident after the first experiments was that vapor phase epitaxy of CdTe on CdTe substrates was difficult to observe because the quality and characteristics of the epilayer were virtually identical to the original substrate. Optical, IR and SEM examination of the surface before and after vapor growth revealed no morphology that could be unambiguously associated with vapor phase epitaxy. However, the fact that epitaxial growth was indeed occurring was proven by the fact that the mass of the substrates increased during growth. No attempt was made to optimize conditions that would lead to better epitaxial growth during the initial stages of the research. Instead it was decided to immediately pursue methods to develop suitable CLEFT growth masks.

B. Development of a Suitable CLEFT Growth Mask - In order to actually cleave the overgrown epilayer it is necessary to identify and optimize an appropriate thin inert growth mask material which can be placed on a CdTe substrate. It was felt that once a suitable mask material was developed, it would be easier to observe epitaxial overgrowth onto the growth mask and optimize the process than to observe epitaxial growth of CdTe on a CdTe substrate.

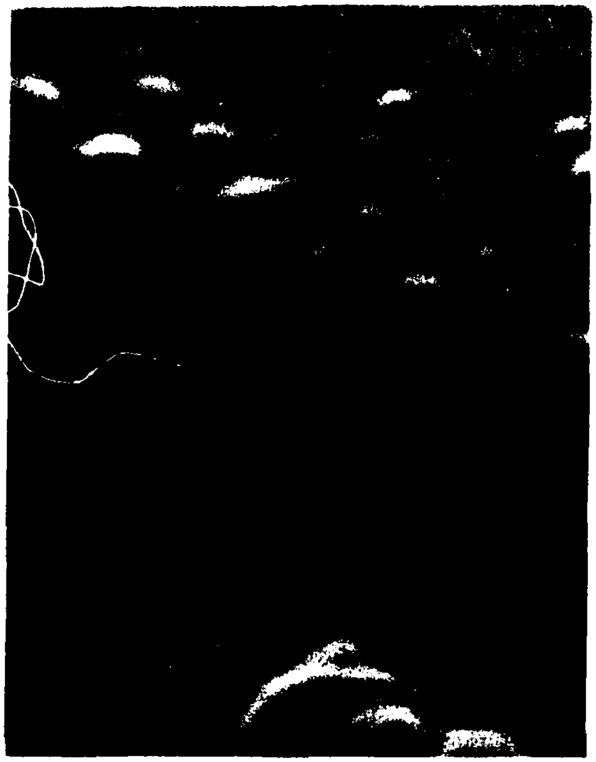
The first efforts at developing a suitable growth mask material

involved emulating the techniques developed at MIT Lincoln Lboratories on GaAs and InP of using carbonized photoresist. Processes were developed to coat CdTe substrates with photoresist and pattern the resist by contact photolithography. Our methods were successful, we could readily reproduce any desired pattern on a thin spincoated resist layer on a CdTe substrate.

Initial attempts at carbonizing the photoresist were unsuccessful. Using the same technique utilized at Lincoln Labs i.e., baking the resist coated substrates in air at elevated temperatures, carbonization was first attempted in air at temperatures ranging from 400 to 800oC for various time intervals. These attempts resulted in deposits that were nonuniform and very difficult to remove from the CdTe substrate. Higher temperatures resulted in the layer being burned away. Baking the resist coated substrates in vacuum at 650oC for 10-20 minutes provided the solution. The carbonized resist layers produced in this way were uniform in appearance and were easily removed from the substrate.

Having developed the capability to deposit carbonized resist on the substrate, a growth experiment was performed using a polycrystalline substrate partially coated with a carbonized resist growth mask. After a 10 hour growth run, the substrate was removed from the ampoule and examined. The appearance of the resist surface had changed markedly (see Figure 3 and 4). This result was originally thought to be due to nucleation of CdTe on pinholes through the carbonized resist surface. Another set of experiments was performed, but this time with much thicker coatings of carbonized photoresist to eliminate possible pinholes. The results were identical, indicating that the nucleation was not taking place simply at pinholes.

Finally, experiments were performed using quartz coated with carbonized resist as the substrate. Again a polycrystalline layer of CdTe was formed the same as with CdTe substrates. Since it is known that the rate of nucleation on quartz was very low, these results indicated that CdTe will readily nucleate from the vapor phase and grow on carbonized photoresist layers yielding polycrytsalline layers of CdTe. For this reason it was decided that carbonized resist was an unacceptable growth mask material and the search for a new material was begun.



1.0 micron

Fig. 3. Carbonized resist coating on CdTe substrate 25kX.
Resist coated area is at upper right.

Fig. 4. Carbonized resist on CdTe after growth run (650X).

An appropriate material was found. The new growth mask material is a liquid solution called "Silicafilm" manufactured by Emulsitone, Inc. This solution produces a thin SiO_2 coating on a substrate after being spun on and heat treated. Initially, difficulties were encountered in the use of Silicafilm on CdTe substrates. When applied according to the manufacturers recommendation, the resultant film fractured and buckled after being exposed to conditions present during VPE growth runs. The film destruction was due to the large difference in thermal expansion characteristics between the CdTe substrate and the SiO_2 coatings. This problem was solved by diluting the Silicafilm solution in an appropriate solvent before application, which resulted in a much thinner film of SiO_2 being formed on the substrate. A series of experiments was performed to determine a dilution ratio that would produce continuous coatings of this material which would not degrade during growth. The resultant SiO_2 coating is readily patterned by etching with dilute HF using a photoresist pattern as an etch mask.

After developing the technique for application of the new growth mask on CdTe, experiments were performed in which unoriented substrates partially coated with SiO_2 were subjected to 16 hour VPE growth runs. Examination of the substrates after the growth revealed that the SiO_2 layer remained uniform and that there was extensive overgrowth of an epitaxial CdTe layer onto the SiO_2 coating.

In the next experiment a radial spoke pattern was applied to an SiO_2 layer on a (111) oriented substrate. Unfortunately, due to problems in obtaining a sufficiently flat substrate surface, the entire pattern was not reproduced on the SiO_2. However a portion of the pattern was well defined and a growth run was performed using this substrate.

The procedure for application of the SiO_2 growth mask is outlined diagrammatically in Figure 5. A portion of a radial spoke patterned SiO_2 mask on a (111)oriented CdTe substrate produced by this method is shown in Figure 6. Although the basic technique for depositing SiO_2 growth masks has worked well, extreme care with substrate surface preparation is required to produce satisfactory results.

C. Investigation of Lateral Overgrowth - Having successfully developed the method for depositing appropriate growth masks, a series of

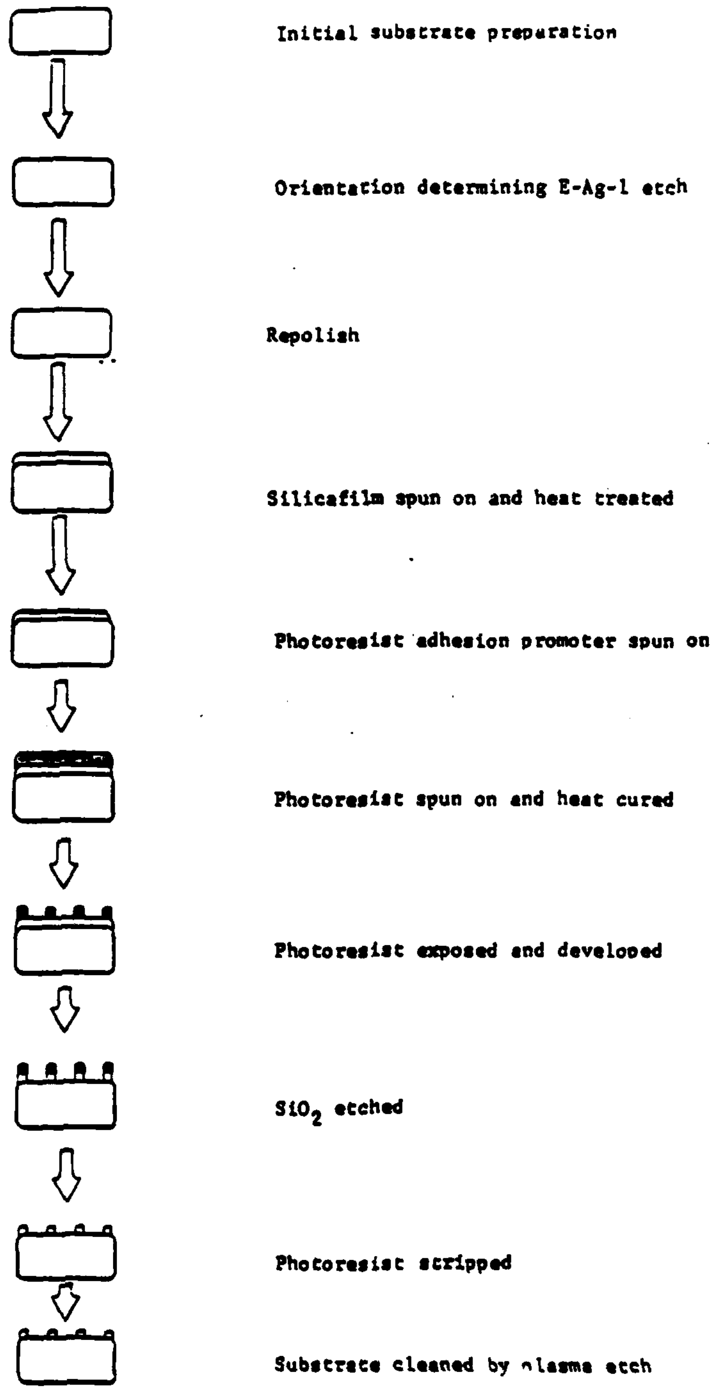


Fig. 5. Schematic of masking procedure.

Fig. 6. Portion of radial growth mask pattern.

investigations was initiated to determine the parameters that effect lateral overgrowth of a CdTe epilayer onto the SiO_2 mask. The first experiments involved applying radial spoke patterns to an unoriented CdTe substrate and performing a 15 hour VPE growth run using these substrates. Examination of the substrates after the run showed that a limited amount of lateral overgrowth of CdTe onto the growth mask had indeed occurred and that there was virtually no nucleation on the SiO_2 masks, both very encouraging results.

The next experiment used the same SiO_2 mask pattern as before, but this time it was applied to the surface of a substrate which was parallel ($\pm$0.75o) to the (111) plane of CdTe. The substrate was subjected to a 16 hr. VPE growth run. Upon removal of the substrate from the growth ampoule, it was observed that on many areas of the film the SiO_2 growth mask was completely overgrown with a CdTe epilayer (Figure 7). It was especially interesting to note that areas where two lateral overgrown films meet there appeared to be no discernable boundary defects indicating that low defect, large area CLEFT films can be produced on appropriately spaced growth masks.

The purpose of utilizing the radial pattern growth mask was to examine the effect of substrate orientation on the lateral to vertical growth rate of the films. Previous work at Lincoln Labs using GaAs and InP had shown a marked dependence of the film growth rate as a function of substrate orientation. In our first experiment to determine the orientation, this effect was indeed observed for CdTe. However, the information was obscured somewhat due to the fact that the entire radial spoke pattern was not reproduced on the substrate because of the aforementioned problems in generating a good SiO_2 mask. For this reason the experiment with the radial spoke pattern had to be repeated several times before a clear picture of the orientation dependence had emerged.

We had originally anticipated correlating the results of the radial mask experiments with x-ray diffration analysis of the substrate to determine which crystallographic orientation led to maximum lateral overgrowth. However by using a selective etch on the substrate surface known as E-Agl* that produced triangular etch pits, it was found that the orientation of the etch pits could be readily correlated with the results

* 14 HNO_3 : 20 H_2O : 4 $K_2Cr_2O_2$: ½ $AgNO_3$ by wt.

100 microns

Fig. 7. SEM showing initial stages of CLEFT growth.

of the experiments with the radial growth mask. Specifically it was found that maximum lateral overgrowth occurred on SiO_2 growth mask stripes that were oriented parallel to the edges of the triangles on the etch pits. The development of the etch pit correlation technique is of great aid in performing experiments with parallel striped SiO_2 growth masks. The use of this technique eliminated the need for time consuming x-ray analysis.

After determining the optimum growth mask angle, an experiment was performed using a parallel striped SiO_2 growth mask on a (111) oriented substrate. After a 48 hr. growth period, the substrate was removed from the ampoule. Examination of the substrate surface showed that some areas of the growth mask were completely overgrown. Unfortunately other areas of the mask had little overgrowth. The reasons for the noncontinuous growth over the entire substrate are not clear although it is probably related to inadequte surface preparation. Despite the sporadic nature of the film growth an attempt was made to cleave a portion of the film. The attempt was unsuccessful due to cleaving of the substrate during the process. In order to remove the film from the substrate without cleaving, it will be necessary to decrease the amount of CdTe connecting the epilayer with the substrate (i.e., increase the proportion of the substrate area covered by the growth mask).

In an effort to improve growth conditions three experiments were performed using different substrate temperatures. Substrate temperatures of 650, 675 and 710oC were tried. The substrates were all (111) oriented with radial stripe growth masks. The results of these experiments showed that an improvement in the lateral to vertical growth rate occurs when the substrate temperature is increased. In addition, an improvement in the uniformity of growth occurred at higher substrate temperatures.

D. <u>Growth of a 1 cm2 CLEFT Film of CdTe</u> - The effort described above culminated in our most successful growth run. A substrate of about 1 cm2 was prepared with a full parallel stripe mask. Using the conditions optimized above, a final growth run was performed. The result was total overgrowth of the substrate by a continuous epilayer of CdTe. The film appeared single crystal and showed no evidence of twins or pin holes. The top surface was not perfectly flat, but as this is the back of the eventual device, this is not considered a problem.

This growth run demonstrates a key condition needed for the CLEFT Process to produce useful CdTe substrates for HgCdTe detectors, namely that CLEFT type lateral overgrowth will occur on (111) oriented CdTe.

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* USGPO: 1983-639-062-1103

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